



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 396 606 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.03.2004 Bulletin 2004/11

(51) Int Cl.7: **E21B 43/267, E21B 43/26**

(21) Application number: **03255474.3**

(22) Date of filing: **02.09.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(72) Inventors:
• **Nguyen, Philip D.**
Duncan, Oklahoma 73533 (US)
• **Barton, Johnny A.**
Marlow, Oklahoma 73055 (US)

(30) Priority: **05.09.2002 US 235352**

(74) Representative: **Wain, Christopher Paul et al**
A.A. Thornton & Co.
235 High Holborn
London WC1V 7LE (GB)

(71) Applicant: **Halliburton Energy Services, Inc.**
Duncan, Oklahoma 73536 (US)

(54) **Fracturing subterranean zones**

(57) Subterranean zones are fractured using a fracturing fluid containing proppant particles coated with a furfuryl alcohol resin composition. The coated proppant particles are deposited in the fractures and the resin

coating hardens by heat to consolidate the proppant particles into chemical and thermal degradation resistant permeable packs.

BEST AVAILABLE COPY

EP 1 396 606 A2

Description

[0001] The present invention relates to methods of forming one or more fractures in a high temperature subterranean zone and consolidating proppant particles therein.

[0002] Hydrocarbon producing wells are often stimulated by hydraulic fracturing treatments. In hydraulic fracturing, a viscous fracturing fluid which also functions as a carrier fluid is pumped into a subterranean zone to be fractured at a rate and pressure such that one or more fractures are formed in the zone. Proppant particles, e.g., graded sand, for propping the fractures open are suspended in the fracturing fluid so that the proppant particles are deposited in the fractures when the fracturing fluid is broken. That is, a viscosity breaker is included in the fracturing fluid whereby the fracturing fluid reverts to a thin fluid which is returned to the surface. The proppant particles deposited in the fractures function to prevent the fractures from closing so that conductive channels are formed through which produced hydrocarbons can readily flow.

[0003] In order to prevent the subsequent flow-back of the proppant particles as well as loose or incompetent fines with fluids produced from the subterranean zone, the proppant particles have heretofore been coated with a hardenable resin composition which is caused to harden and consolidate the proppant particles in the zone. However, when the subterranean zone has a temperature above about 375°F, the hardened resin composition and the permeable proppant particle packs consolidated therewith rapidly deteriorate which allows proppant particles and formation fines to flow-back with produced formation fluids. The flow-back of the proppant particles and formation fines is very detrimental in that it erodes metal goods, plugs piping and vessels and causes damage to valves, instruments and other production equipment.

[0004] Another problem encountered in the use of prior hardenable resin compositions for coating proppant particles is that the hardenable resin composition or components thereof have had short shelf lives. In addition, the hardenable resin composition components have heretofore had low flash points, i.e. flash points of about 60°F or below, making them very dangerous to use. Also, when the prior hardenable resin compositions or components thereof have been stored at high ambient temperatures, the compositions or components have quickly hardened making them unsuitable for use.

[0005] Thus, there are needs for improved methods of consolidating proppant particles in subterranean fractures whereby the permeable packs of consolidated proppant particles formed are chemical and thermal degradation resistant at high temperatures, i.e. temperatures above about 375°F.

[0006] In one aspect, the present invention provides a hardenable resin composition for coating proppant particles and which hardens by heat, which composition comprises a hardenable resin comprised of furfuryl alcohol resin; furfuryl alcohol; a solvent for said resin having a flash point above 125°F; a silane coupling agent; and a surfactant for facilitating the coating of said hardenable resin composition on said proppant particles and for causing said hardenable resin composition to flow to the contact points between adjacent resin coated proppant particles.

[0007] The invention also provides a method of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above 200°F, which method comprises pumping a gelled liquid fracturing fluid into said subterranean zone, said fluid containing proppant particles coated with a hardenable resin composition suspended therein, to form one or more fractures and to deposit said proppant particles therein; and allowing said hardenable resin composition on said resin composition coated proppant particles to harden by heat and consolidate said proppant particles into one or more chemical and thermal degradation resistant permeable packs; wherein said resin composition is according to the invention.

[0008] The method of the present invention for forming one or more fractures in a subterranean zone having a temperature above about 200°F penetrated by a well bore and consolidating proppant particles therein may comprise the following steps. Proppant particles coated with a hardenable resin composition are provided. The hardenable resin composition is comprised of furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin, a silane coupling agent, optionally, a hydrolyzable ester for breaking gelled fracturing fluid films on the proppant particles, and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent coated proppant particles. A gelled liquid fracturing fluid is also provided which is pumped into the subterranean zone to form one or more fractures and to deposit the proppant particles therein. The proppant particles coated with the hardenable resin composition are mixed with the fracturing fluid being pumped whereby the proppant particles coated with the hardenable resin composition are suspended therein. When the proppant particles coated with the hardenable resin composition have been deposited in the one or more fractures formed, the pumping of the fracturing fluid and the mixing of the proppant particles coated with the hardenable resin composition with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the resin composition coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0009] Another improved method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above

about 200°F is comprised of the following steps. A liquid hardenable resin composition is provided comprised of furfuryl alcohol resin, furfuryl alcohol, an ethylene glycol butyl ether solvent for the resin, an n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane coupling agent, optionally, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate esters and a C₁₂-C₂₂ alkyl phosphate surfactant. A source of dry proppant particles and a gelled liquid
 5 fracturing fluid comprised of water and a gelling agent selected from the group consisting of guar gum, guar gum derivatives and cellulose derivatives are also provided. The gelled liquid fracturing fluid is pumped into the subterranean zone to form the one or more fractures therein and to place the proppant particles therein. The hardenable resin composition is coated onto the dry proppant particles conveyed from the source thereof to form hardenable resin composition coated proppant particles. The hardenable resin composition coated proppant particles are mixed with the fracturing
 10 fluid pumped into the subterranean zone whereby the hardenable resin composition coated proppant particles are suspended therein. When the hardenable resin composition coated proppant particles have been placed in the one or more fractures formed in the subterranean zone, the pumping of the gelled fracturing fluid, the coating of the hardenable resin composition onto the dry proppant particles and the mixing of the hardenable resin composition coated proppant particles formed with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the
 15 hardenable resin composition coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0010] The present invention provides improved methods of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F comprising the following steps. Proppant particles coated with a hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin, a silane coupling agent, optionally, a hydrolyzable ester for breaking gelled fracturing fluid films on the proppant particles and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent resin coated proppant particles are provided. A gelled liquid fracturing fluid is also provided. The gelled liquid fracturing fluid is pumped into the subterranean zone to form the one or more fractures and to deposit the proppant particles therein.
 20 The proppant particles coated with the hardenable resin composition are mixed with the fracturing fluid pumped into the subterranean zone whereby the proppant particles coated with the hardenable resin composition are suspended therein. When the proppant particles coated with the hardenable resin composition have been deposited in the one or more fractures, the pumping of the gelled liquid fracturing fluid and the mixing of the proppant particles coated with the hardenable resin composition with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the
 25 resin composition coated proppant particles are allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0011] The proppant particles utilized in accordance with the present invention are generally of a size such that formation particulate solids that migrate with produced fluids are prevented from being produced from the subterranean zone. Various kinds of proppant particles can be utilized including graded sand, bauxite, ceramic materials, glass materials, walnut hulls, polymer beads and the like. Generally, the proppant particles have a size in the range of from about 2 to about 400 mesh, U.S. Sieve Series. The preferred proppant is graded sand having a particle size in the range of from about 10 to about 70 mesh, U.S. Sieve Series. Preferred sand particle size distribution ranges are one or more of 10-20 mesh, 20-40 mesh, 40-60 mesh or 50-70 mesh, depending on the particular size and distribution of formation solids to be screened out by the consolidated proppant particles.
 35

[0012] Furfuryl alcohol resins are readily available from a number of commercial sources. For example, suitable furfuryl alcohol resin is commercially available from Durez Corporation under the trade designation "Durez 33682™". Upon curing by heat in a subterranean zone, the furfuryl alcohol resin forms an insoluble mass that is highly resistant to chemical attack and thermal degradation, i.e., the cured resin resists thermal degradation at temperatures up to 700°F. The furfuryl alcohol resin is generally present in the hardenable resin composition in an amount in the range of from about 40% to about 75% by weight of the composition and more preferably in an amount of from about 55% to about 65%.
 40

[0013] The furfuryl alcohol is generally present in the hardenable resin composition in an amount in the range of from about 1 % to about 20% by weight of the composition and more preferably in an amount of from about 5% to about 15%.
 45

[0014] Examples of solvents for the furfuryl alcohol resin which have flash points above about 125°F and can be utilized include, but are not limited to, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, diethyleneglycol methyl ether, ethyleneglycol butyl ether, diethyleneglycol butyl ether, dimethyl formamide, propylene carbonate, butyl acetate, furfuryl acetate, d'limonene and fatty acid methyl esters. Of these, ethyleneglycol butyl ether is preferred. The solvent is included in the hardenable resin composition in an amount in the range of from about 10% to about 40% and more preferably in an amount of about 15% to about 30%.
 50

[0015] Examples of silane coupling agents which can be utilized in the hardenable resin composition include, but are not limited to, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane and n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane. Of these, n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane is
 55

preferred. The silane coupling agent is included in the hardenable resin composition in an amount in the range of from about 0.1 % to about 3% by weight of the composition and more preferably in an amount of from about 0.5% to about 2%.

[0016] Examples of hydrolyzable esters which can optionally be included in the hardenable resin composition include, but are not limited to, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, sorbitol, catechol, dimethylthiolate, methyl salicylate, dimethylsuccinate and tertbutylhydroperoxide. Of these, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate are preferred. The hydrolyzable ester is included in the liquid hardenable resin composition in an amount in the range of from about 0% to about 3% by weight of the composition and more preferably in an amount of about 1.5%.

[0017] Encapsulated sodium bisulfate can optionally be used as a substitute for the hydrolyzable esters. Encapsulated sodium bisulfate in the amount ranging from 1% to 15% by weight of the resin composition is admixed with the proppant slurry during coating of resin mixture onto the proppant. The sodium bisulfate must be encapsulated to minimize its release and interaction with the gelled liquid fracturing fluid during pumping of the fracturing fluid and proppant into the subterranean zone. Without encapsulation, the sodium bisulfate prematurely breaks down the fracturing fluid and causes the proppant to settle which is undesirable during the fracturing treatment.

[0018] Surfactants for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent resin coated proppant particles utilized in the hardenable resin composition include, but are not limited to, ethoxylated nonyl phenol phosphate ester surfactants, mixtures of one or more cationic surfactants and one or more non-ionic surfactants and a C_{12} — C_{22} alkyl phosphonate surfactant. Of these, a C_{12} — C_{22} alkyl phosphonate surfactant is preferred. The surfactant or surfactants utilized are included in the hardenable resin composition in an amount in the range of from about 1 % to about 15% by weight of the composition and more preferably in an amount of about 5% to about 10%.

[0019] Another improved method of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F is comprised of the following steps. A liquid hardenable resin composition is provided comprised of furfuryl alcohol resin, furfuryl alcohol, an ethylene glycol butyl ether solvent for the resin, an n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane coupling agent, optionally, a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, esters and a C_{12} — C_{22} alkyl phosphate surfactant. A source of dry proppant particles and a gelled liquid fracturing fluid are also provided. The gelled liquid fracturing fluid is comprised of water and a gelling agent selected from the group consisting of guar gum, guar gum derivatives and cellulose derivatives. The gelled liquid fracturing fluid is pumped into the subterranean formation to form the one or more fractures therein and to place the proppant particles therein. The hardenable resin composition is coated onto the dry proppant particles conveyed from the source thereof to form hardenable resin composition coated proppant particles. The hardenable resin composition coated proppant particles are mixed with the fracturing fluid being pumped whereby the hardenable resin composition coated proppant particles are suspended therein. When the hardenable resin composition coated proppant particles have been placed in the one or more fractures by the fracturing fluid, the pumping of the fracturing fluid, the coating of the hardenable resin composition onto the dry proppant particles and the mixing of the hardenable resin composition coated proppant particles formed with the fracturing fluid are terminated. Thereafter, the hardenable resin composition on the hardenable resin composition coated proppant particles is allowed to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0020] The furfuryl alcohol resin, the furfuryl alcohol, the solvent, the silane coupling agent, the hydrolyzable ester mixture, and the surfactant that make up the liquid hardenable resin composition are present in the composition in the same amounts as described above.

[0021] The water in the gelled liquid fracturing fluid is selected from the group consisting of fresh water and salt water. The term "salt water" is used herein to mean unsaturated salt solutions and saturated salt solutions including brines and seawater.

[0022] The gelling agent in the fracturing fluid is generally present in an amount in the range of from about 0.1 % to about 2% by weight of water therein and more preferably in an amount of about 0.2% to about 1 %.

[0023] The gelled liquid fracturing fluid can include a cross-linking agent for increasing the viscosity of the fracturing fluid. Examples of suitable cross-linking agents include, but are not limited to, alkali metal borates, borax, boric acid and compounds capable of releasing multivalent metal ions in aqueous solutions. When used, the cross-linking agent is included in the fracturing fluid in an amount in the range of from about 0.01% to about 2% by weight of water therein and more preferably in an amount of about 0.1 % to about 1%.

[0024] The fracturing fluid generally also includes a delayed viscosity breaker which functions to reduce the viscosity of the fracturing fluid and cause the resin composition coated proppant particles suspended in the fracturing fluid to be deposited in the fractures. Examples of delayed viscosity breakers which can be utilized include, but are not limited to, alkali metal and ammonium persulfates which are delayed by being encapsulated in a material which slowly releases the breaker, alkali metal chlorites, alkali metal hypochlorites and calcium hypochlorite. When used, the delayed viscosity breaker is included in the fracturing fluid in an amount in the range of from about 1% to about 5% by weight of water

therein.

[0025] The hardenable resin composition of this invention for coating proppant particles and which hardens by heat is basically comprised of a furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin having a flash point above about 125°F, a silane coupling agent, optionally, a hydrolyzable ester for breaking gelled fracturing fluid films and a surfactant for facilitating the coating of the hardenable resin composition on the proppant particles and for causing the hardenable resin composition to flow to the contact points between adjacent resin coated proppant particles.

[0026] The furfuryl alcohol resin, the furfuryl alcohol, the solvent, the silane coupling agent, the hydrolyzable ester and the surfactant are as described above in connection with the methods of this invention and are present in the hardenable resin composition in the amounts set forth above.

[0027] The hardenable resin composition of this invention can be stored at high ambient temperatures for long periods of time without hardening or otherwise deteriorating.

[0028] An improved method of this invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F is comprised of the steps of: (a) providing proppant particles coated with a hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, a solvent for the resin, a silane coupling agent and a surfactant for facilitating the coating of the resin on the proppant particles and for causing the resin to flow to the contact points between adjacent resin coated proppant particles; (b) providing a gelled liquid fracturing fluid; (c) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures and to deposit the proppant particles therein; (d) mixing the proppant particles coated with the hardenable resin composition with the fracturing fluid pumped in accordance with step (c) whereby the proppant particles coated with the hardenable resin composition are suspended therein; (e) terminating steps (c) and (d) when the proppant particles coated with the hardenable resin composition have been deposited in the one or more fractures; and; (f) allowing the hardenable resin composition on the resin composition coated proppant particles to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0029] Another improved method of the present invention for forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above about 200°F is comprised of the steps of: (a) providing a liquid hardenable resin composition comprised of furfuryl alcohol resin, furfuryl alcohol, an ethylene glycol butyl ether solvent for the resin having a flash point above about 125°F, an n-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane coupling agent and a C₁₂—C₂₂ alkyl phosphate surfactant; (b) providing a source of dry proppant particles; (c) providing a gelled liquid fracturing fluid comprised of water and a gelling agent selected from the group consisting of guar gum, guar gum derivatives and cellulose derivatives; (d) pumping the gelled liquid fracturing fluid into the subterranean zone to form the one or more fractures therein and to place the proppant particles therein; (e) coating the hardenable resin composition onto the dry proppant particles conveyed from the source thereof to form hardenable resin composition coated proppant particles; (f) mixing the hardenable resin composition coated proppant particles formed in step (e) with the fracturing fluid pumped in accordance with step (d) whereby the hardenable resin composition coated proppant particles are suspended therein; (g) terminating steps (d), (e) and (f) when the hardenable resin composition coated proppant particles have been placed in the one or more fractures; and (h) allowing the hardenable resin composition on the hardenable resin composition coated proppant particles to harden by heat and consolidate the proppant particles into one or more chemical and thermal degradation resistant permeable packs.

[0030] A hardenable resin composition of this invention for coating proppant particles comprises: a hardenable resin comprised of furfuryl alcohol resin; furfuryl alcohol; a solvent for the resin having a flash point above about 125°F; a silane coupling agent; and a surfactant for facilitating the coating of the hardenable resin composition on the proppant particles and for causing the hardenable resin composition to flow to the contact points between adjacent resin coated proppant particles.

[0031] In order to further illustrate the methods and compositions of this invention, the following examples are given.

Example 1

Effect of Time and Temperature on Viscosity of Mixed Resin

[0032] Furfuryl alcohol resin ("Durez 33682™") obtained from the Durez Corporation was mixed with 1% of a silane coupling agent and 5% of an alkyl phosphate surfactant by weight of the furfuryl alcohol resin. The viscosity of the resin mixture was monitored with time at room temperature and at 120°F in an oven, using a Brookfield DV-II viscometer and spindle No. 3. The temperature of 120°F was selected to simulate the storage temperature in a warehouse during the summer months. Table I shows the recorded viscosities of the resin mixtures at different time periods. The results indicate that the viscosities of the resin mixtures remained substantially unchanged with time, even at higher temperature.

TABLE I

Days	Viscosity (cp) of Resin Mixture Measured at Room Temperature	Viscosity (cp) of Resin Mixture Measured at 120 °F
0	1395	-
4	2765	-
5	2586	-
13	2982	-
18	2675	448
19	2555	576
21	2406	640
26	2624	717
32	2701	666
55	2995	730
90	2675	680

Example 2

Consolidation Testing - Effect of Cure Time and Temperature

[0033] 300 grams of 20/40-mesh bauxite proppant were dry coated with 9.0 mL of the resin mixture (3% by weight of proppant) before mixing in 360 mL of 35 lbs/Mgal carboxymethylhydroxypropyl guar based fracturing fluid. The resin coated proppant slurry was then placed in a heat bath to bring the slurry temperature to 180°F. While stirring, 0.72 mL of an oxidizer breaker (2 gal/Mgal) and 0.126 mL of zirconium crosslinker (0.35 gal/Mgal) was added to the slurry. The content was stirred continuously at 180°F for one hour to simulate the effect of pumping. The slurry was then packed into brass chambers. The proppant packs were cured in an oven at different cure periods ranging from 3 hours to 7 days and at temperatures ranging from 250°F to 350°F without applying closure stress on the proppant packs. After each curing duration, the brass chambers containing the proppant packs were removed from the oven and allowed to cool down to room temperature. Cores were obtained from the consolidated proppant packs for unconfined compressive strength (UCS) measurements at room temperature. Table II shows the UCS values of the consolidated proppant cores. The results indicate that the unconfined compressive strengths of the proppant packs increases with cure time and begins to level off after 24 hour cure times. The mixed resin in the Series II testing contained encapsulated sodium bisulfate.

TABLE II

Cure Temperatures	UCS (psi) Measured at Room Temperature After Various Curing Periods						
Series I	3 hrs	4 hrs	5 hrs	6 hrs	24 hrs	48 hrs	7 days
300°F	-	-	-	-	89	487	1298
325°F	19	58	214	428	1306	-	1593
350°F	-	-	-	106	1052	1223	1740
Series II	3 hrs	4 hrs	5 hrs	6 hrs	24 hrs	48 hrs	7 days
275°F	NA	-	-	-	145	-	-
300°F	NA	-	-	25	274	422	1003
325°F	80	-	-	361	1261	1561	1642
350°F	146	-	-	817	1313	-	1624

Claims

1. A hardenable resin composition for coating proppant particles and which hardens by heat, which composition comprises a hardenable resin comprised of furfuryl alcohol resin; furfuryl alcohol; a solvent for said resin having a flash point above 125°F; a silane coupling agent; and a surfactant for facilitating the coating of said hardenable resin composition on said proppant particles and for causing said hardenable resin composition to flow to the

contact points between adjacent resin coated proppant particles.

2. A composition according to claim 1, wherein said furfuryl alcohol resin is present in an amount of from 40% to 75% by weight of said composition.
3. A composition according to claim 1 or 2, wherein said furfuryl alcohol is present in said hardenable resin composition in an amount of from 1% to 20%.
4. A composition according to claim 1, 2, or 3, wherein said solvent for said resin having a flash point above 125°F is dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, dimethyl formamide, diethylene glycol methyl ether, ethylene glycol butyl ether, diethylene glycol butyl ether, propylene carbonate, butyl acetate, furfuryl acetate, d'limonene or a fatty acid methyl esters.
5. A composition according to any of claims 1 to 4, wherein said solvent for said resin having a flash point above 125°F, is present in an amount of from 10% to 40% by weight of said composition.
6. A composition according to any of claims 1 to 5, wherein said silane coupling agent is N-2-(aminoethyl)-3-amino-propyltrimethoxysilane, 3-glycidoxypopyltrimethoxysilane or n-beta-(aminoethyl)-gamma-aminopropyl- trimethoxysilane.
7. A composition according to any of claims 1 to 6, wherein said silane coupling agent is present in said liquid hardenable resin composition in an amount of from 0.1% to 3% by weight of said composition.
8. A composition according to any of claims 1 to 7, which further comprises a hydrolyzable ester for breaking gelled fracturing fluid films on said proppant particles.
9. A composition according to claim 8, wherein said hydrolyzable ester is selected from the group consisting of a mixture of dimethylglutarate, dimethyladipate and dimethylsuccinate, sorbitol, catechol, dimethylthiolate, methyl salicylate, dimethylsuccinate and tertbutylhydroperoxide.
10. A composition according to claim 9, wherein said hydrolyzable ester is present in said hardenable resin composition in an amount up to 3%.
11. A composition according to any of claims 1 to 10, wherein said surfactant comprises at least one member selected from ethoxylated nonyl phenol phosphate ester, mixtures of one or more cationic surfactants and one or more non-ionic surfactants and a C₁₂-C₂₂ alkyl phosphonate surfactant.
12. A composition according to any of claims 1 to 11, wherein said surfactant is present in an amount of from 1% to 15%, preferably from 4% to 8%, by weight of said composition.
13. A composition according to any of claims 1 to 12, wherein said proppant particles are graded sand.
14. A method of forming one or more fractures in a subterranean zone penetrated by a well bore and consolidating proppant particles therein, the subterranean zone having a temperature above 200°F, which method comprises pumping a gelled liquid fracturing fluid into said subterranean zone, said fluid containing proppant particles coated with a hardenable resin composition suspended therein, to form one or more fractures and to deposit said proppant particles therein; and allowing said hardenable resin composition on said resin composition coated proppant particles to harden by heat and consolidate said proppant particles into one or more chemical and thermal degradation resistant permeable packs; wherein said resin composition is as claimed in any of claims 1 to 13.
15. A method according to claim 14, wherein dry proppant particles have been coated with said resin composition; and wherein said gelled liquid fracturing fluid comprises water and a gelling agent selected from guar gum, guar gum derivatives and cellulose derivatives.
16. A method according to claim 14 or 15, wherein said gelling agent is present in said fracturing fluid in an amount of from 0.2% to 1% by weight of water therein.
17. A method according to claim 14, 15 or 16, wherein said gelled liquid fracturing fluid further comprises a cross-

linking agent selected from alkali metal borates, borax, boric acid and compounds capable of releasing multivalent metal ions in aqueous solutions.

5 **18.** A method according to claim 17, wherein said cross-linking agent is present in said fracturing fluid in an amount of from 0.2% to 1% by weight of water therein.

10 **19.** A method according to any of claims 14 to 18, wherein said gelled liquid fracturing fluid further comprises a delayed viscosity breaker selected from alkali metal and ammonium persulfates which are delayed by being encapsulated in a material which slowly releases said breaker, alkali metal chlorites, alkali metal hypochlorites and calcium hypochlorites.

15 **20.** A method according to claim 19, wherein said delayed viscosity breaker is present in said fracturing fluid in an amount of from 1% to 5% by weight of water therein.

15

20

25

30

35

40

45

50

55

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 396 606 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
01.09.2004 Bulletin 2004/36

(51) Int Cl.7: **E21B 43/267, E21B 43/26**

(43) Date of publication A2:
10.03.2004 Bulletin 2004/11

(21) Application number: **03255474.3**

(22) Date of filing: **02.09.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(72) Inventors:
• **Nguyen, Phillip D.**
Duncan, Oklahoma 73533 (US)
• **Barton, Johnny A.**
Marlow, Oklahoma 73055 (US)

(30) Priority: **05.09.2002 US 235352**

(74) Representative: **Wain, Christopher Paul et al**
A.A. Thornton & Co.
235 High Holborn
London WC1V 7LE (GB)

(71) Applicant: **Halliburton Energy Services, Inc.**
Duncan, Oklahoma 73536 (US)

(54) Fracturing subterranean zones

(57) Subterranean zones are fractured using a fracturing fluid containing proppant particles coated with a furfuryl alcohol resin composition. The coated proppant particles are deposited in the fractures and the resin

coating hardens by heat to consolidate the proppant particles into chemical and thermal degradation resistant permeable packs.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 5474

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCL7)
E	EP 1 394 355 A (HALLIBURTON ENERGY SERV INC) 3 March 2004 (2004-03-03) * paragraph '0006! - paragraph '0010! * * paragraph '0013! - paragraph '0014! * * paragraph '0016! - paragraph '0019! * * paragraph '0026! - paragraph '0035! *	1,4-19	E21B43/267 E21B43/26
X,P	EP 1 326 003 A (HALLIBURTON ENERGY SERV INC) 9 July 2003 (2003-07-09) * paragraph '0006! *	1,5-13, 15-19	
Y,P	* paragraph '0011! - paragraph '0012! * * paragraph '0015! - paragraph '0019! * * paragraph '0024! - paragraph '0029! *	4,14	
Y	US 3 492 147 A (YOUNG BILL M ET AL) 27 January 1970 (1970-01-27) * column 2, line 11 - line 39 * * column 3, line 72 - column 4, line 48; examples II, III * * column 7, line 55 - column 8, line 21 *	1-4,6, 13,14	
Y	US 4 785 884 A (ARMBRUSTER DAVID R) 22 November 1988 (1988-11-22) * column 3, line 37 - column 4, line 40 * * column 5, line 25 - column 6, line 14 *	1-4,6, 13,14	TECHNICAL FIELDS SEARCHED (InCL7) E21B
Y	EP 0 864 726 A (HALLIBURTON ENERGY SERV INC) 16 September 1998 (1998-09-16) * column 3, line 36 - column 4, line 35 * * column 5, line 28 - column 7, line 2 * * column 7, line 18 - line 39 *	1,4,6, 13-15, 17,19	
Y	EP 1 130 215 A (HALLIBURTON ENERGY SERV INC) 5 September 2001 (2001-09-05) * paragraph '0012! - paragraph '0013! * * paragraph '0029! - paragraph '0038! *	1,4,6, 13-15, 17,19	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 July 2004	Examiner Boulon, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 25 5474

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-07-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1394355	A	03-03-2004	US 2004040713 A1	04-03-2004
			CA 2436453 A1	28-02-2004
			EP 1394355 A1	03-03-2004
EP 1326003	A	09-07-2003	US 2003131998 A1	17-07-2003
			CA 2415814 A1	08-07-2003
			EP 1326003 A1	09-07-2003
			NO 20030043 A	09-07-2003
			US 2003131999 A1	17-07-2003
			US 2003188872 A1	09-10-2003
US 3492147	A	27-01-1970	NONE	
US 4785884	A	22-11-1988	CA 1330257 C	21-06-1994
EP 0864726	A	16-09-1998	US 5791415 A	11-08-1998
			CA 2232051 A1	13-09-1998
			DE 69820138 D1	15-01-2004
			DE 69820138 T2	27-05-2004
			DK 864726 T3	22-03-2004
			EP 0864726 A2	16-09-1998
EP 1130215	A	05-09-2001	NO 981102 A	14-09-1998
			US 6257335 B1	10-07-2001
			AU 769119 B2	15-01-2004
			AU 2315101 A	06-09-2001
			BR 0100806 A	06-11-2001
			CA 2336439 A1	02-09-2001
			EP 1130215 A2	05-09-2001
			NO 20011061 A	03-09-2001

20

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)